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Title: Impedance/Dielectric Spectroscopy and Theory/Engineering Implications

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Impedance/Dielectric Spectroscopy and Theory/Engineering Implications

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LDRD Project 20190057DR
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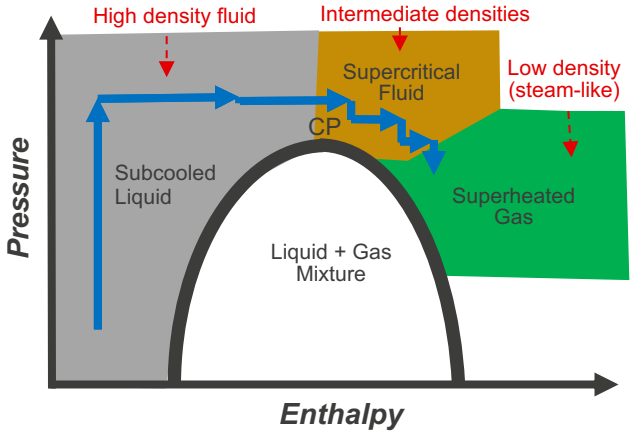
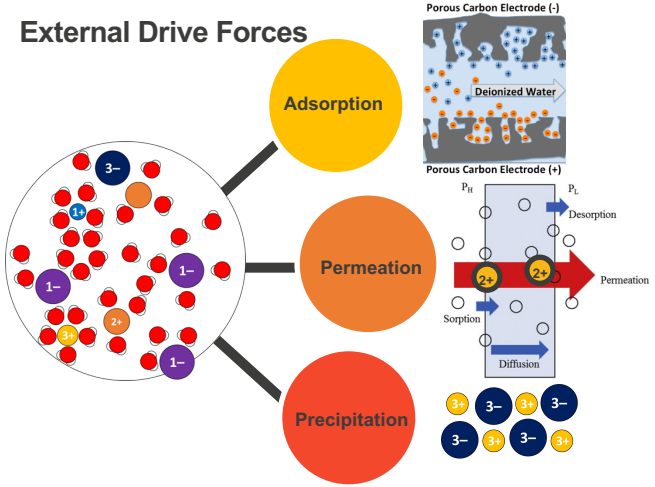
Motivation

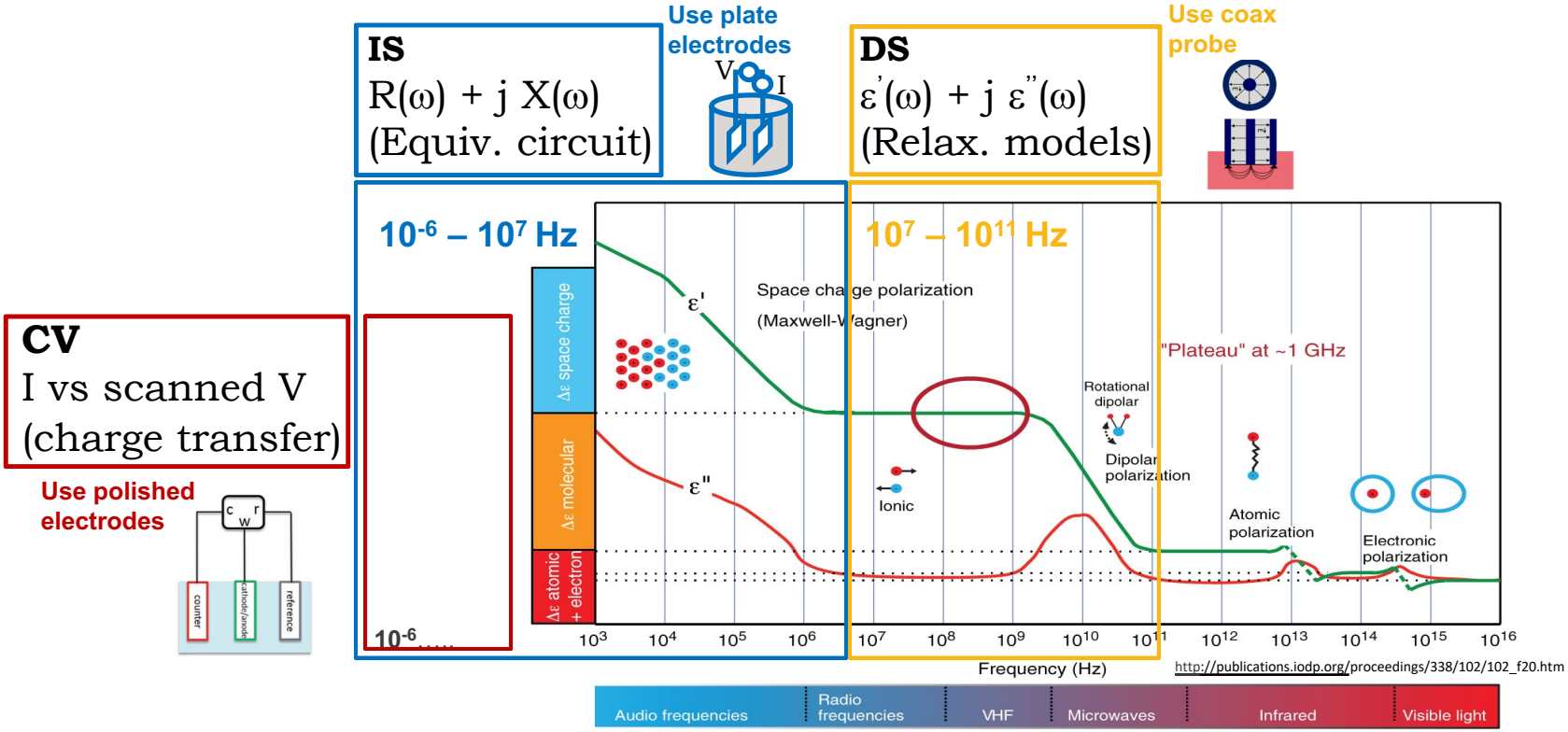
- Impedance Spectroscopy (**IS**), Dielectric Spectroscopy (**DS**), and Cyclic Voltammetry (**CV**)
  1) to understand **ion structure** and **properties** in water in **large P/T-phase space**
  2) for **in situ diagnostics** and **monitoring** in **batch** and **flow processes**
  3) (with **electrodes**) to apply **external drive forces** for **selective ion removal**





Introduction - I

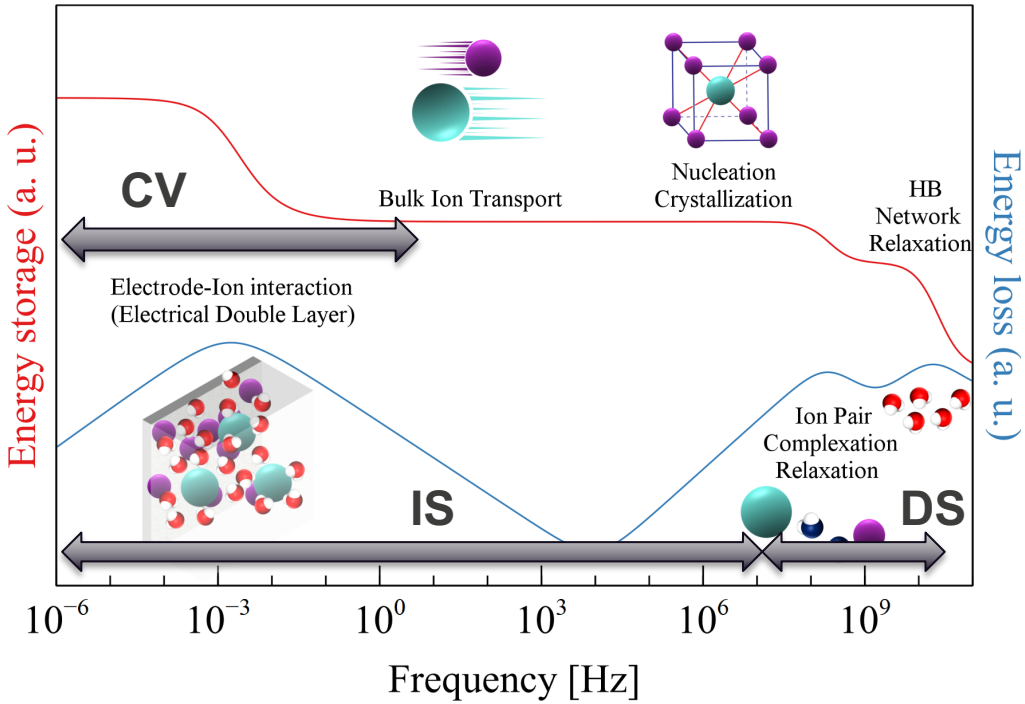
- Impedance Spectroscopy (**IS**), dielectric spectroscopy (**DS**), and Cyclic Voltammetry (**CV**) method description



Introduction - II

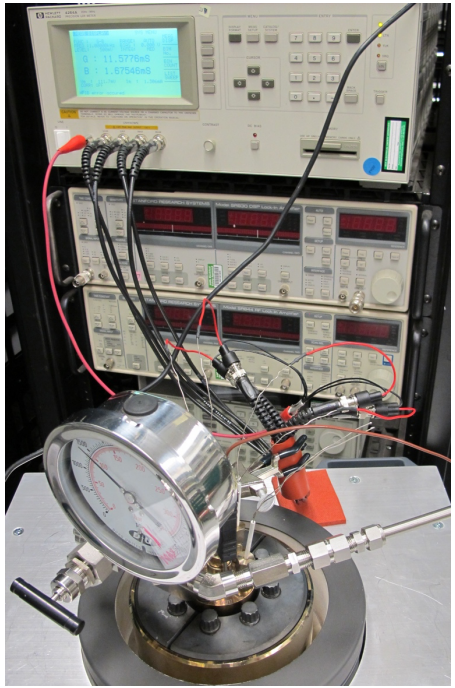
- To understand ion structure and properties in aqueous solutions:
  - combine **spectroscopic** and **electrochemical methods** with **modeling**

Experiment	Modeling
Ambient conditions (pre-/post-treatment)	Statistical mechanics (Alcorn, Velizhanin)
Elevated temp./press. (pre-/post-treatment)	Monte Carlo (MC) Tech. (Patel, Maerzke, Yoon)
High temp./pressures (sub-/super-critical water desalination)	Molecular Dynamics (MD) Techniques (Yoon, Patel, Maerzke)

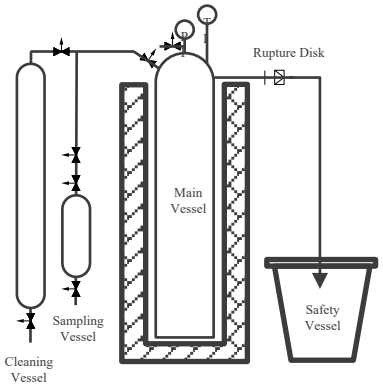


Introduction - III

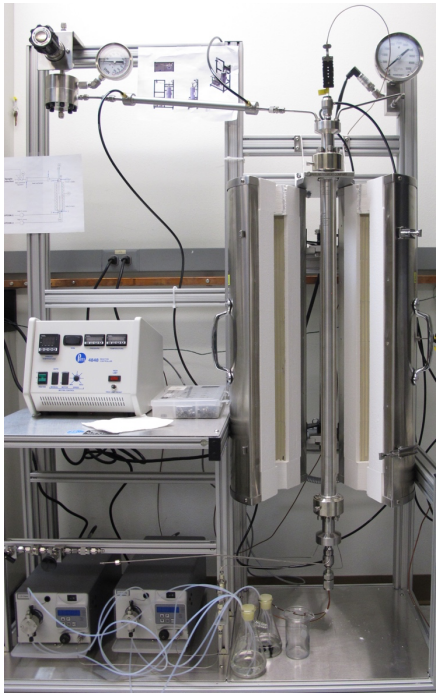
- Use spectroscopic and electrochemical methods for **in situ diagnostics** and **monitoring** in **batch** and **flow processes**



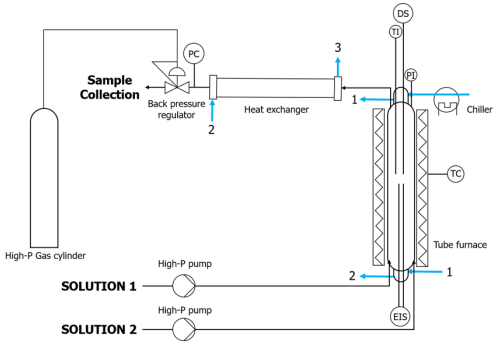
Batch System



- 5000 psi, 500 °C
- In situ sampling
- In situ IS and DS



Flow System



- 5000 psi, 550 °C
- Two solution mixing
- In flow sampling
- In situ IS and DS

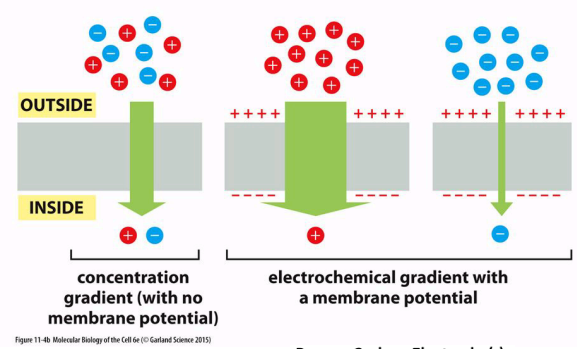
Introduction - IV

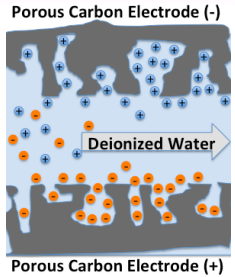
❒ Application of **external drive forces** for **selective ion removal**:

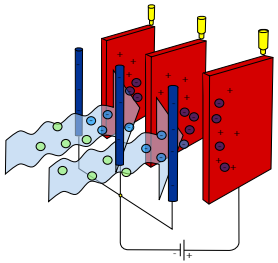
- Faradaic (e.g., redox absorption) and Non-Faradaic (e.g., electrostatic adsorption) effects
- Large-area and/or functionalized electrodes or transfer media
- External drive induced/controlled adsorption, absorption, or permeation
- External drive induced/controlled precipitation enhancement/inhibition

Possible paths:

- **Electric field effects on ion transport** (e.g., electric field across membrane)
- **Electrostatic ion removal** (e.g., CDI, MCDI)
- **Electric field driven nucleation/growth** (e.g., Electrostatic precipitator for salts)







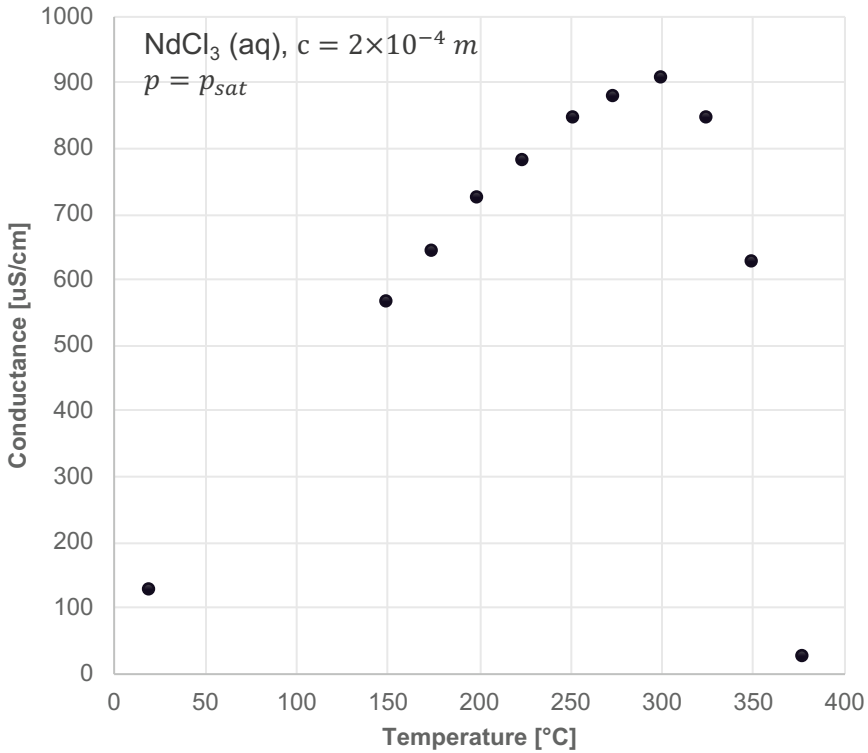
R&D Approach & Current Status

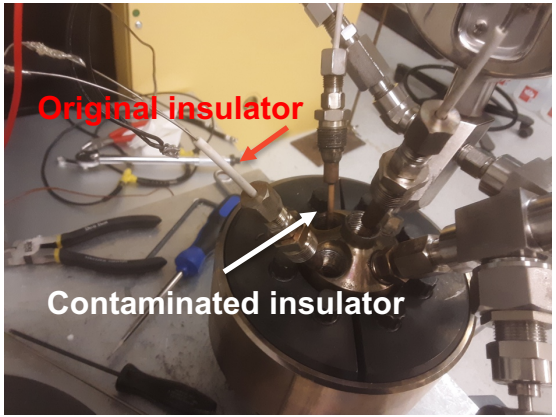
Experimental Conditions	IS		DS		CV		Ext. Force	
	EXP.	SIM.	EXP.	SIM.	EXP.	SIM.	EXP.	SIM.
Ambient Conditions	✓	✓	✓	✓	✓	✓	✓	✓
Elevated P and T	✓	✓	✓	✓	✓	✓	✓	✓
Near/supercritical	✓	✓	✓	✓			✓	✓
Batch System	✓	✓	✓	✓			✓	✓
Flow System	✓	✓	✓	✓			✓	✓

- ☐ Build experimental capability (✓), test in ambient conditions; cross-validate with theoretical predictions and MC/MD simulation results (✓). In progress (✓)
- ☐ Develop high temperature/pressure in situ electrodes that are corrosion resistant; cross-validate with theory/simulations
- ☐ Implement in batch and flow systems for diagnostics/monitoring
- ☐ Search for external field effects for enhanced or ion-selective desalination

Project Outcomes - I

- **Specific conductance measurement of $NdCl_3$ (aq) at elevated temperature and pressure**

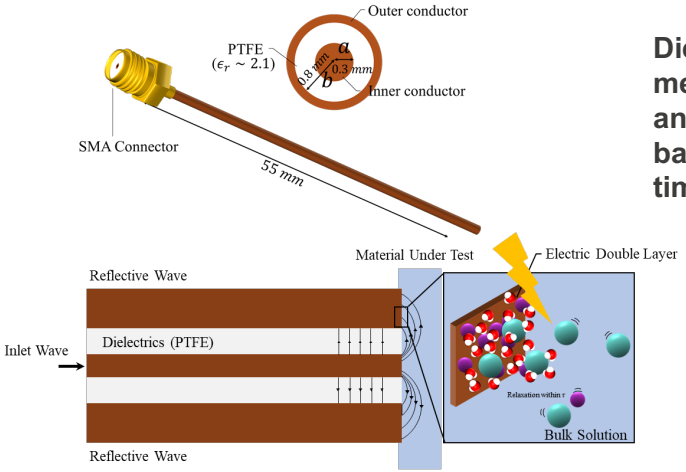




- Implemented IS capability and numerical algorithms to extract the conductance
- Specific conductance shows a maximum as Yoon showed in the MD simulations
- Different ion pairing behavior observed in $NdCl_3$ vs NaCl solutions at the same concentration

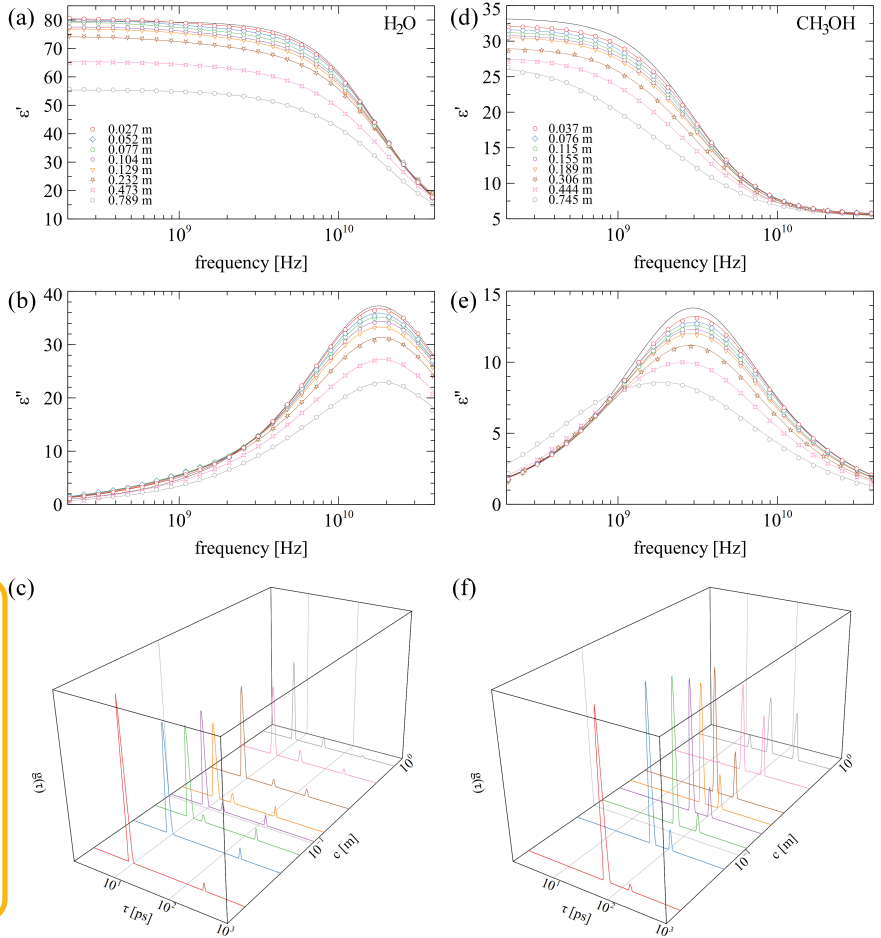
Project Outcomes - II

❒ DS of $NdCl_3$ in water and methanol



Principles behind the reflection measurement technique

Dielectric spectrum measurement results and its decomposition based on relaxation time distribution



- ❒ Challenging to implement DS in high-pressure/ high-temperature cell
- ❒ Demonstrated the suitability of the method to study ion cluster/complexation behavior
- ❒ Implemented capability and algorithms for DS measurement of variety of liquids

Project Outcomes - III

❒ Publications

Experiment/Modeling:
"Electrical conductivity, ion pairing, and ion self-diffusion in aqueous NaCl solutions at elevated temperatures and pressures,"
Yoon, T. J., Patel, L. A., Vigil, M. J., Maerzke, K. A., Findikoglu, A. T., & Currier, R. P. (2019)., J. Chem. Phys., 151(22), 224504.

Dielectric Spectroscopy (DS):
"Dielectric relaxation of neodymium chloride in water and in methanol,"
Yoon, T. J., Vigil, M. J., Raby, E. Y., Singh, R. P., Maerzke, K. A., Currier, R. P. & Findikoglu, A. T. (2020), J. Mol. Liq. (under revision)

Impedance Spectroscopy (IS):
"Specific conductance of $NdCl_3$ in water along the vapor-liquid equilibrium,"
Yoon, T. J., Vigil, M. J., Sharan, P., Singh, R. P., Maerzke, K. A., Currier, R. P. & Findikoglu, A. T. (2020), J. Chem. Eng. Data (in preparation)

Summary of Outcomes and Future Work

- Built experimental capabilities (IS, DS, CV) and tested them in ambient conditions, and cross-validated them with theoretical predictions and results of MC/MD simulations
- Developed high-temperature/high-pressure in situ electrodes/probes that are corrosion resistant, and are in the process of deploying them in our batch and flow reactors
- Demonstrated the ability to use external drive forces (qE) to remove ions from simple salt solutions both experimentally and numerically
- Future work will include spectroscopic and MD/MC studies of multi-salt systems, implementations in batch and flow reactors, and investigations of the use of external drive forces for enhanced/selective separation of ions from complex salt solutions